LETTER TO THE EDITOR

Multiphoton detachment from negative ions: new theory vs experiment

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Abstract.   In this paper we compare the results of our adiabatic theory (Gribakin and Kuchiev, *Phys. Rev. A*, submitted for publication) with other theoretical and experimental results, mostly for halogen negative ions.   The theory is based on the Keldysh approach.   It shows that the multiphoton detachment rates and the corresponding n-photon detachment cross sections depend only on the asymptotic parameters A and κ of the bound state radial wave function $R(r) \simeq Ar^{-1}e^{-\kappa r}$. The dependence on κ is very strong.   This is the main reason for the disagreement with some previous calculations, which employ bound state wave functions with incorrect asymptotic κ values.   In a number of cases our theoretical results produces best agreement with absolute and relative experimental data.

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In this paper we use the theory of multiphoton detachment from negative ions developed in our previous work (Gribakin and Kuchiev 1996) to calculate n-photon detachment cross sections and excess photon detachment (EPD) spectra for some negative ions and frequencies, which have been explored experimentally.

It has been shown that for a linearly polarized light the differential n-photon detachment cross section for the electron in the initial state lm is

$$\frac{\mathrm{d}\sigma_n^{(lm)}}{\mathrm{d}\Omega} = \frac{pA^2\omega(2l+1)}{4\pi^2\sqrt{2n\omega}} \frac{(l-|m|)!}{(l+|m|)!} \left|P_l^{|m|}\left(\sqrt{1+p_\perp^2/\kappa^2}\right)\right|^2 \left(\frac{\pi e}{nc\omega^2}\right)^n$$
$$\times \frac{\exp(p_\parallel^2/\omega)}{\sqrt{\kappa^2+p_\perp^2}}\left[1+(-1)^{n+l+m}\cos\Xi\right] , \tag{1}$$

where κ is determined by the initial energy of the electron $E_0 \equiv -\kappa^2/2$, $p = \sqrt{2n\omega-\kappa^2}$ is the photoelectron momentum, $p_\parallel = p\cos\theta$ and $p_\perp = p\sin\theta$ are its components parallel and perpendicular to the field, $c \approx 137$ is the speed of light, $e = 2.71\ldots$, $P_l^{|m|}$ is the associated Legendre function, and

$$\Xi = (2n+1)\tan^{-1}\frac{p_\parallel}{\sqrt{\kappa^2+p_\perp^2}} + \frac{p_\parallel\sqrt{\kappa^2+p_\perp^2}}{\omega} . \tag{2}$$

is the phase which determines the oscillatory pattern of the photoelectron angular distribution. This effect is due to interference between the two contributions to the photodetachment amplitude produced at the moments of time when the field strength reaches its maximum (there are two such instants in every period of the field). The phase Ξ varies with the ejection angle of the photoelectron in between $-\Xi_0$ and Ξ_0, where $\Xi_0 = (2n+1)\tan^{-1}(p/\kappa) + p\kappa/\omega$, and can be quite large, even for the lowest-n process, $p \sim \sqrt{\omega}$, $\Xi_0 \sim \sqrt{n}$. Note that in accordance with the general symmetry properties, the cross section is zero at $\theta = \pi/2$, when $n+l+m$ is odd.

After the electron detachment from a closed-shell negative ion the neutral atom is left in either of the two fine-structure states with the total angular momentum $j = l\pm\frac{1}{2}$, e.g., $^2P_{3/2}$ and $^2P_{1/2}$ for halogens. In this case the n-photon detachment cross section summed over the projections of the angular momentum is given by

$$\frac{\mathrm{d}\sigma_n^{(j)}}{\mathrm{d}\Omega} = \frac{2j+1}{2l+1}\sum_{m=-l}^{l}\frac{\mathrm{d}\sigma_n^{(lm)}}{\mathrm{d}\Omega} , \tag{3}$$

where different values of κ and binding energies $|E_0|$ should be used for $j = l\pm\frac{1}{2}$, since the two sublevels have different detachment thresholds. The main contribution to the sum in equation (3) comes from $m = 0$, since these orbitals are extended along the direction of the field.

The sum over m can be carried out analytically, taking into account the fact that $P_l^{|m|}$ in equation (1) is a function of the imaginary angle ϑ, $\cos\vartheta = \sqrt{1+p_\perp^2/\kappa^2}$, so that

$\left[P_l^{|m|}(\cos\vartheta)\right]^* = (-1)^m P_l^{|m|}(\cos\vartheta)$. The result is

$$\frac{\mathrm{d}\sigma_n^{(j)}}{\mathrm{d}\Omega} = \frac{pA^2\omega(2j+1)}{4\pi^2\sqrt{2n\omega}}\left(\frac{\pi e}{nc\omega^2}\right)^n \frac{\exp(p_\parallel^2/\omega)}{\sqrt{\kappa^2+p_\perp^2}}\left[P_l\left(1+2p_\perp^2/\kappa^2\right)+(-1)^{n+l}\cos\Xi\right]\;, \qquad (4)$$

where P_l is the Legendre polynomial, $P_0(x)=1$, $P_1(x)=x$, etc.

The total n-photon detachment cross section $\sigma_n^{(j)}$ is obtained by integrating equation (4) over the emission angles of the photoelectron. The result can be presented in the following form

$$\sigma_n^{(j)} = (2j+1)\frac{pA^2}{4\pi n}\left(\frac{\pi e}{nc\omega^2}\right)^n F_{nl}(p^2/2\omega)\;, \qquad (5)$$

where F_{nl} is a universal function of the photoelectron energy in the units of ω,

$$F_{nl}(\varepsilon) = \int_{-1}^{1}\frac{e^{2\varepsilon x^2}}{\sqrt{1-\varepsilon x^2/n}}\left\{P_l\left(1+\frac{2\varepsilon(1-x^2)}{n-\varepsilon}\right)+\right.$$

$$\left.+(-1)^{n+l}\cos\left[(2n+1)\tan^{-1}\left(\frac{x\sqrt{\varepsilon}}{\sqrt{n-\varepsilon x^2}}\right)+2x\sqrt{\varepsilon(n-\varepsilon x^2)}\right]\right\}\mathrm{d}x\;. \qquad (6)$$

Despite a somewhat cumbersome look, this dimensionless function is easy to calculate, and we present it for $l=0,1$, $n=2$–9 in figure 1. Note the different behaviour of F_{nl} at small ε, which provides a correct threshold law $\sigma\propto p$, or $\sigma\propto p^3$, for even and odd $n+l$, respectively. This depends on whether the lowest photoelectron partial wave is s or p. Equations (4) and (5) and figure 1 predict a variety of properties for the photodetachment from all negative ions.

The theory which has lead to equations (1) and (4) shows that the detachment process takes place when the electron is far from the atomic core, at distances estimated as $r\sim\kappa^{-1}\sqrt{2n}$ (Gribakin and Kuchiev 1996). This is why the probabilities can be expressed in terms of the asymptotic parameters A and κ of the bound-state wave function. All corrections due to electron-atom scattering or electron correlations, e.g., the electron-atom polarizational interaction, are expected to be suppressed by some powers of n.

Equation (5) enables one to make simple estimates of saturation intensities I_S defined as $\sigma_n^{(j)}(I_\mathrm{S}/\omega)^n\tau = 1$, where τ is the laser pulse duration,

$$I_\mathrm{S} = \frac{nc\omega^3}{\pi e}\left[\frac{4\pi n}{(2j+1)pA^2F_{nl}\tau}\right]^{1/n}\;. \qquad (7)$$

For low photoelectron energies $p^2/2\sim\omega$, $F_{nl}\sim 1$, the n-dependence of I_S is basically determined by the first factor with $\omega\approx|E_0|/n$,

$$I_\mathrm{S}\propto n^{-2}. \qquad (8)$$

This dependence was first noticed in the numerical calculations by Crance (1988).

In what follows we use equations (4) and (5) to calculate the cross section for those negative ions and photon frequencies where some experimental data are available. Parameters of the electron bound state wave functions in these negative ions are listed in table 1. Note that if after the detachment the neutral atom is left in its ground state, then κ is determined by the corresponding electron affinity E_a (Hotop and Lineberger 1985), $\kappa = \sqrt{2E_a}$, and if the atom in the final state is excited (e.g., to the upper fine-structure level), then $\kappa = \sqrt{2(E_a + \Delta)}$, where Δ is the energy of the atomic excitation (Radtsig and Smirnov 1986). In both cases we are dealing with the detachment of the valence electron, hence, the same value of A is used. In contrast with κ, the values of A for most ions are known only to within 10 % or worse. In spite of the fact that the present theory is strictly valid for large n, it will be applied to n as low as 2, where, we believe, it gives reasonable answers.

Table 1. Parameters of the negative ions used to calculate the n-photon detachment cross sections.

Ion	Term	Atom	l	j	A^a	κ
O^-	^2P	^3P	1	0.5^b	0.65	0.328
Cu^-	$^1S_0$	$^2S_{1/2}$	0	0.5	1.2	0.301
Ag^-	$^1S_0$	$^2S_{1/2}$	0	0.5	1.3	0.3094
Au^-	$^1S_0$	$^2S_{1/2}$	0	0.5	1.3	0.4119
F^-	$^1S_0$	$^2P_{3/2}$	1	1.5	0.7	0.4998
F^-	$^1S_0$	$^2P_{1/2}$	1	0.5	0.7	0.5035
Cl^-	$^1S_0$	$^2P_{3/2}$	1	1.5	1.3	0.5156
Cl^-	$^1S_0$	$^2P_{1/2}$	1	0.5	1.3	0.5233
Br^-	$^1S_0$	$^2P_{3/2}$	1	1.5	1.4	0.4973
Br^-	$^1S_0$	$^2P_{1/2}$	1	0.5	1.4	0.5300
I^-	$^1S_0$	$^2P_{3/2}$	1	1.5	1.8	0.4742
I^-	$^1S_0$	$^2P_{1/2}$	1	0.5	1.8	0.5423

[a]Values taken from Radtsig and Smirnov (1986) for O^-, Cu^-, Ag^-, and Au^-, and from Smirnov and Nikitin (1988) for F^-, Cl^-, Br^-, and I^-.
[b]This value gives correct cross sections for oxygen, when the fine-structure is neglected.

Figure 2(a) presents a comparison of the 2-photon detachment cross sections for O^-, Cu^-, Ag^- and Au^- measured by Stapelfeldt *et al* (1991a, 1991b) at $\omega = 1.165$ eV, with our values, and the theoretical result of Robinson and Geltman (1967) for O^-. In the latter calculation the single-electron wave functions were calculated in a model polarization potential chosen to reproduce the correct value of the electron affinity. Figure 2(b) shows the 3-photon cross sections for F^-, Br^- and I^-, as measured by Blondel *et al* (1989) and Kwon *et al* (1989) (F^- only), together with the results of our calculations and those of Crance (1988), where the Hartree-Fock (HF) wave

functions and plane waves were used to describe the initial and the final state of the electron, respectively. Two features are most obvious. First, our theoretical values are considerably higher than the experimental ones, and second, there is a much better agreement between the relative cross sections, as given by the theory and experiment. There is also a reasonable agreement between the two calculations for O^-, Br^- and I^-.

The large disagreement between our value for F^- and that of Crance 1988 is, as discussed in Gribakin and Kuchiev (1996), due to the incorrect behaviour of the HF bound state wave function, which falls off much faster than the true one (the HF value of κ for F^- is 0.6, vs the true $\kappa = 0.5$). Note that among the halogen negative ions this discrepancy is the largest for F^-. Accordingly, the theoretical cross sections for Br^- and I^- are in better agreement (HF values of $\kappa = 0.528$, 0.508 respectively; compare to the true values of $\kappa = 0.497$, 0.474 for $j = \frac{3}{2}$, see table 1). It is worth pointing out that the calculations for halogens that employed HF wave functions of the photoelectron (Crance 1987a, 1987b) produced cross sections close to those obtained within the plane-wave approximation. From the point of view of our theory this is a consequence of the importance of large distances for the multiphoton detachment. Therefore, we have to conclude that the agreement that the theoretical and experimental values had enjoyed for F^- was probably coincidental, caused by the significant error in the previous calculations. On the other hand, the relative magnitudes of the cross sections for F^-, Br^- and I^- given by our theory are very close to the measured ones.

The minimal number of quanta needed for the detachment of Cl^- at the Nd:YAG laser frequency is four. In this instance the calculated value $\sigma_4 = 10.2 \times 10^{-124}$ cm^{8}s^3 is also greater than the experimental $\sigma_4 = 0.97^{+0.68}_{-0.41} \times 10^{-124}$ cm^{8}s^3 (Blondel and Trainham 1989), as well as that by Crance (1988), $\sigma_4 = 5.6 \times 10^{-124}$ cm^{8}s^3. In order to compare the results for all four halogens at this frequency, one can calculate the saturation intensities I_S for some τ, e.g., $\tau = 2\pi/E_a$, as in Blondel and Trainham 1989. Using our cross sections and the data from Blondel and Trainham 1989 we complete table 2. The

Table 2. Saturation intensities for the multiphoton detachment of the halogen negative ions by $\omega = 1.165$ eV linearly polarized light.

Ion	n	τ	I_S^{exp}	I_S^{theor}	$R = I_S^{exp}/I_S^{theor}$
		fs	10^{13} W/cm^2	10^{13} W/cm^2	
F^-	3	1.22	4.4	2.50	1.76
Cl^-	4	1.14	3.2	1.79	1.79
Br^-	3	1.23	3.2	1.72	1.86
I^-	3	1.35	2.4	1.23	1.95

existing discrepancy between the theory and experiment is characterised by the ratio R, which remains almost constant, $R \approx 1.8$–1.9.

In a more recent work by Davidson *et al* (1992) the 2- and 3-photon detachment cross sections for Cl$^-$ by 2 eV photons have been measured. Their value $\sigma_2 = 16^{+29}_{-8} \times 10^{-50}$ cm^{4}s is in good agreement with ours, $\sigma_2 = 9.44 \times 10^{-50}$ cm^{4}s, whereas the values predicted by other theories are notably smaller, $\sigma_2 = 5.5 \times 10^{-50}$ cm^{4}s (Crance 1987), and $\sigma_2 = 2.5 \times 10^{-50}$ cm^{4}s (Jiang and Starace 1987). Our cross section also agrees with the result of a much earlier measurement by Trainham *et al* 1987 at a smaller photon energy, $\omega = 1.874$ eV, $\sigma_2 = 1.3 \pm 0.9 \times 10^{-50}$ cm^{4}s (experiment), $\sigma_2 = 2.19 \times 10^{-50}$ cm^{4}s (theory). The result of Robinson and Geltman (1967) is $\sigma_2 = 1.68 \times 10^{-50}$ cm^{4}s. The 3-photon cross sections from Davidson *et al* (1992), $\sigma_3 = 1.84^{+6.3}_{-1.2} \times 10^{-82}$ cm^{6}s^2, is also close to our calculation, $\sigma_3 = 10.35 \times 10^{-82}$ cm^{6}s^2.

In the earlier experimental work devoted to the EPD Davidson *et al* (1991) measured the ratio between the 5-photon and 4-photon detachment signals in Cl$^-$ at $\omega = 1.165$ eV. If the energy of the laser pulse is below the saturation limit, then for a pulse with a Gaussian spatial and temporal profile this ratio is given by $\left(\frac{4}{5}\right)^{3/2}(\sigma_5/\sigma_4)I/\omega$, where I the peak intensity in the pulse. Indeed, the experimental points in figure 3 of Davidson *et al* 1991 display an approximately linear dependence on the intensity. The corresponding slope can be estimated as 0.0415, if the intensity is in units of 10^{12} W/cm^2, which is quite close to our theoretical estimate of 0.0466. When the cross sections of Crance 1988 are used, a value of 0.053 is obtained. The difference between our theory and that based on the HF description of the negative ion is not as large for the ratio of the cross sections, as it is for the cross sections themselves. At the peak intensity of 2.4×10^{12} W/cm^2, well into the saturation regime, we calculated the ratio of 4- and 6-photon detachments to be 120, with the experimental value between 70 and 200.

The EPD was also measured for Au$^-$, where 2-, 3-, and possibly 4-photon detachment signals were observed at $\omega = 1.165$ eV (Stapelfeldt *et al* 1991). However, the interpretation of that experiment is not straightforward, because already at $\frac{1}{15}$ of the maximal laser intensity of 3×10^{12} W/cm^2 achieved in that experiment the $n = 2$ channel is closed due to the ponderomotive threshold shift.

Equation (4) can be used to calculate angular distributions of photoelectrons studied by Blondel *et al* (1991,1992) and Dulieu *et al* (1995). For the 2-photon detachment from halogen negative ion at $\omega = 2.331$ eV the shapes of the differential cross sections from equation (4) are close to those produced by the 'HF + plane-wave' calculations presented in figure 3 of Blondel *et al* 1992, the difference in the absolute values aside. They reproduce well the features of the experimental data. In some cases our calculations are in better agreement with the experiment, e.g., for Cl$^-$, Br$^-$ ($^2P_{3/2}$ final state), or F$^-$, see figure 3. Note that for F$^-$ the analytical result (4) is also in good agreement with the numerical calcultions of Pan and Starace (1991), where electron correlations in the initial, intermediate and final states of the 2-photon process have been taken into account. The largest discrepancy between the theory and experiment is observed for I$^-$.

Similar conslusions can be drawn from the comparison of our angular distributions at $\omega = 1.165$ eV (figure 3 of Gribakin and Kuchiev 1996) with the experimental results for F^-, $n = 3, 4$, 5, Cl^-, $n = 4$, Br^-, $n = 3$, and I^-, $n = 3$ (Blondel *et al* 1991, Dulieu *et al* 1995). Overall, the simple analytical expression (4) reproduces remarkably well the complicated oscillatory pattern of the photoelectron angular distributions.

In summary, our theory of multiphoton detachment in a strong laser field (Gribakin and Kuchiev 1996) yields very simple formulae for the n-photon detachment cross sections and photoelectron angular distributions. Apart from ω and n they depend only on the electron orbital angular momentum l and the two constants A and κ which characterize the behaviour of the bound-state wave function at large distances. The correct asymptotic behaviour of the bound-state wave fucntion at large distances is crucial for obtaining correct absolute values of the n-photon cross sections. The fact that the theory is based on the properties of the wave function at large separations from the atom make it very reliable. At the same time the simple structure of our final results permits make quick estimates of the cross sections for any negative ion. We have applied the theory to the negative ions and processes studied experimentally, and found that our results are in reasonable, and in some cases, very good agreement with the experimental data. Some discrepancies found call for more accurate absolute experimental values. When more sophisticated calculations are performed, our formulae can be used as a benchmark, to demonstrate the role of various possible corrections, which are expected be small for the processes considered. Of course, there are other processes where many-electron correlations play a decisive role, e.g., multiple photodetachment or ionization (Kuchiev 1987, 1995, 1996).

Acknowledgments

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Figure captions

Figure 1. Dependence of the universal function $F_{nl}(\varepsilon)$ on the photoelectron energy in units of ω for the n-photon detahcment of s $(l = 0)$ and p $(l = 1)$ electrons, for $n = 2, \ldots, 9$ (values of n label curves in the plots). The different behaviour of $F_{nl}(\varepsilon)$ at small photoelectron energies $\varepsilon \ll 1$ ensures correct threshold behaviour of the n-photon detachment cross section, $\sigma_n \propto \varepsilon^{1/2}$ for even $n + l$, and $\sigma_n \propto \varepsilon^{3/2}$ for odd $n + l$.

Figure 2. Comparison of the theoretical and experimental n-photon detachment cross sections at $\omega = 1.165$ eV. (a) $n = 2$, ■ , our calculation; □ , calculation by Robinson and Geltman (1967), ● , experiment by Stapelfeldt *et al* (1991). (b) $n = 3$, ■ , our calculation; □ , calculation by Crance (1988); ● , experiment by Blondel *et al* (1989); ○ , experiment by Kwon *et al* (1989).

Figure 3. Normalized differential 2-photon detachment cross sections $4\pi\sigma^{-1}\mathrm{d}\sigma/\mathrm{d}\Omega$ for F^- at $\omega = 2.33$ eV. Experimental results by Blondel *et al* (dots) taken from Pan and Starace (1991), and close to those given in Blondel *et al* (1992); —— , our calculation (sum of the $j = 3/2$ and $j = 1/2$ cross sections).
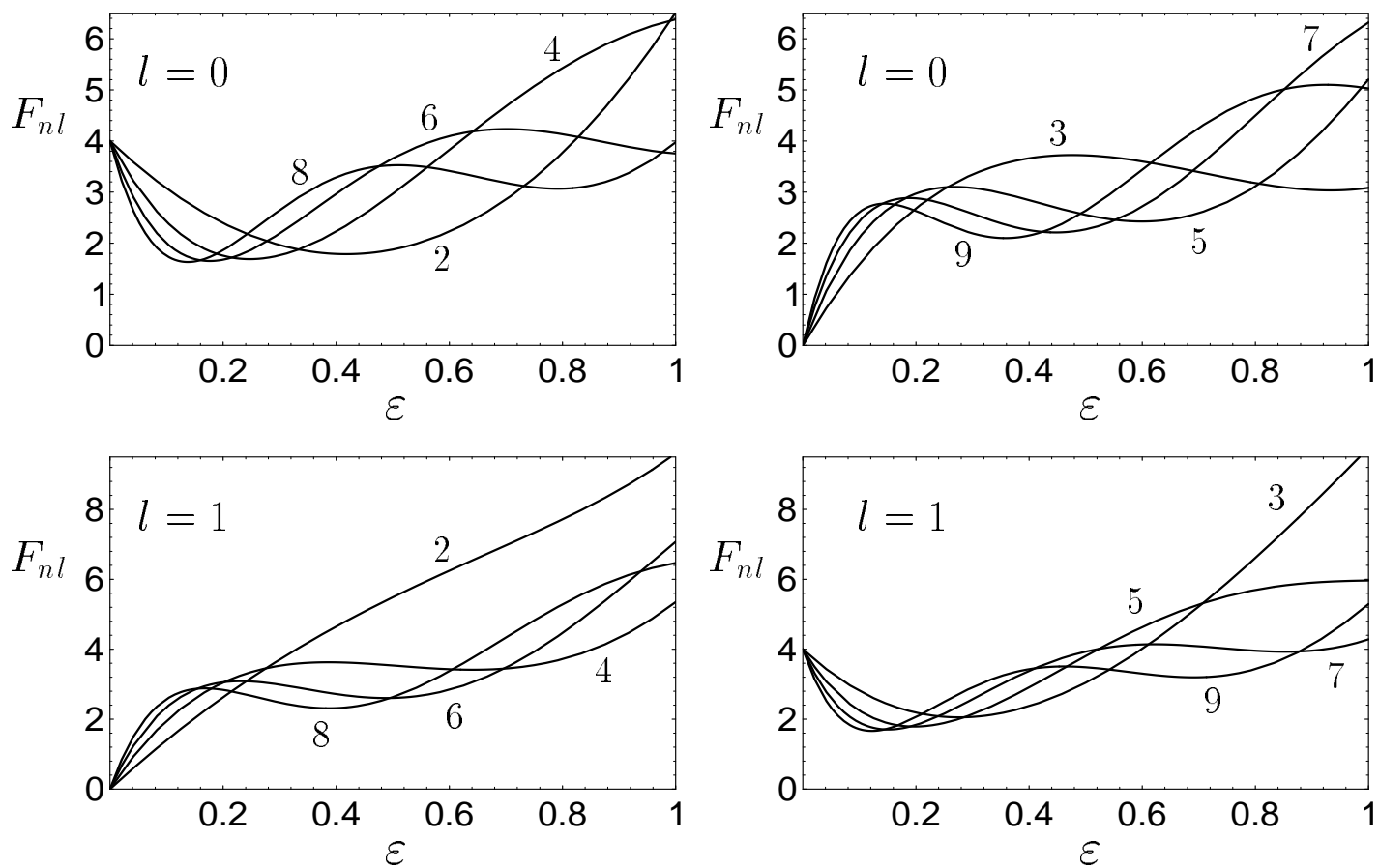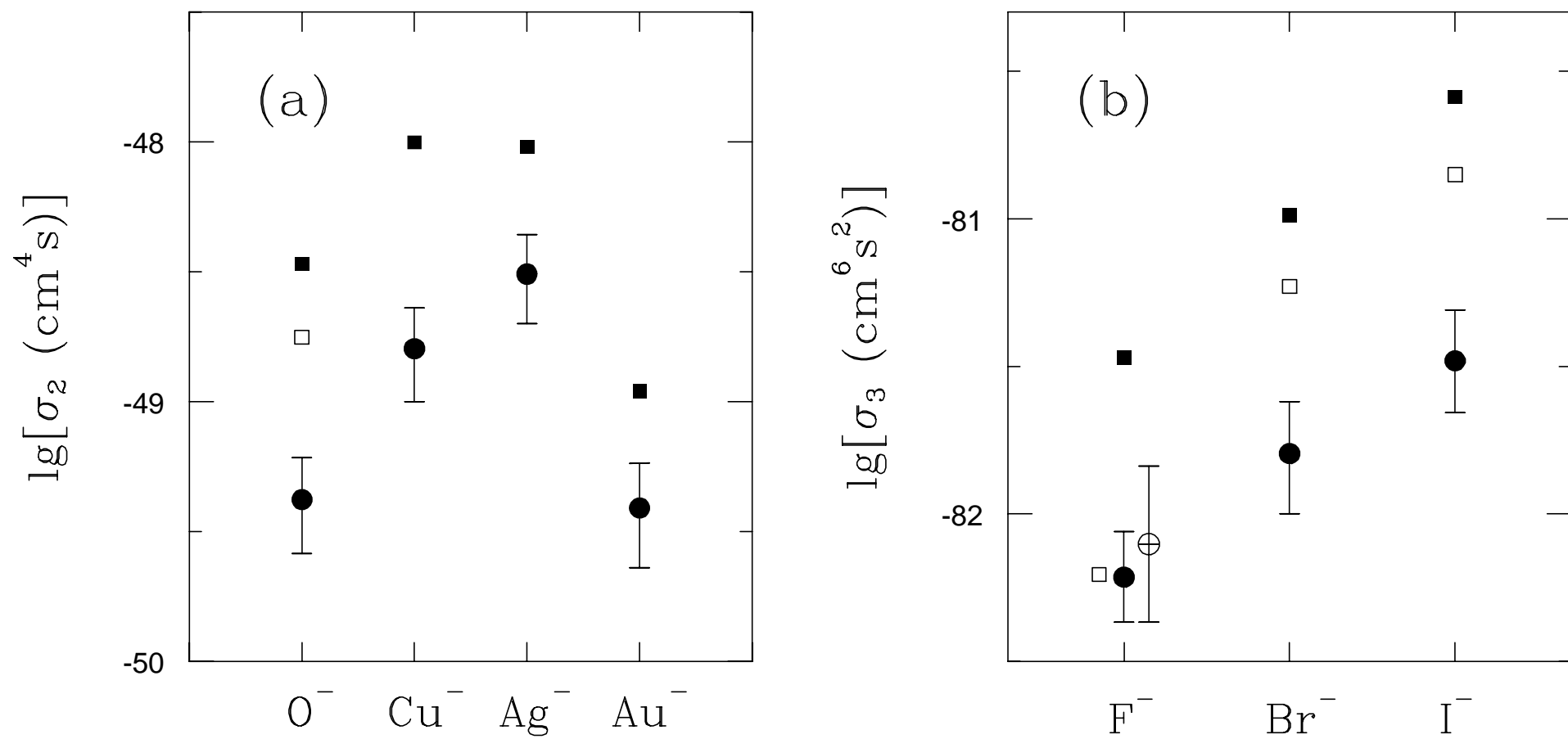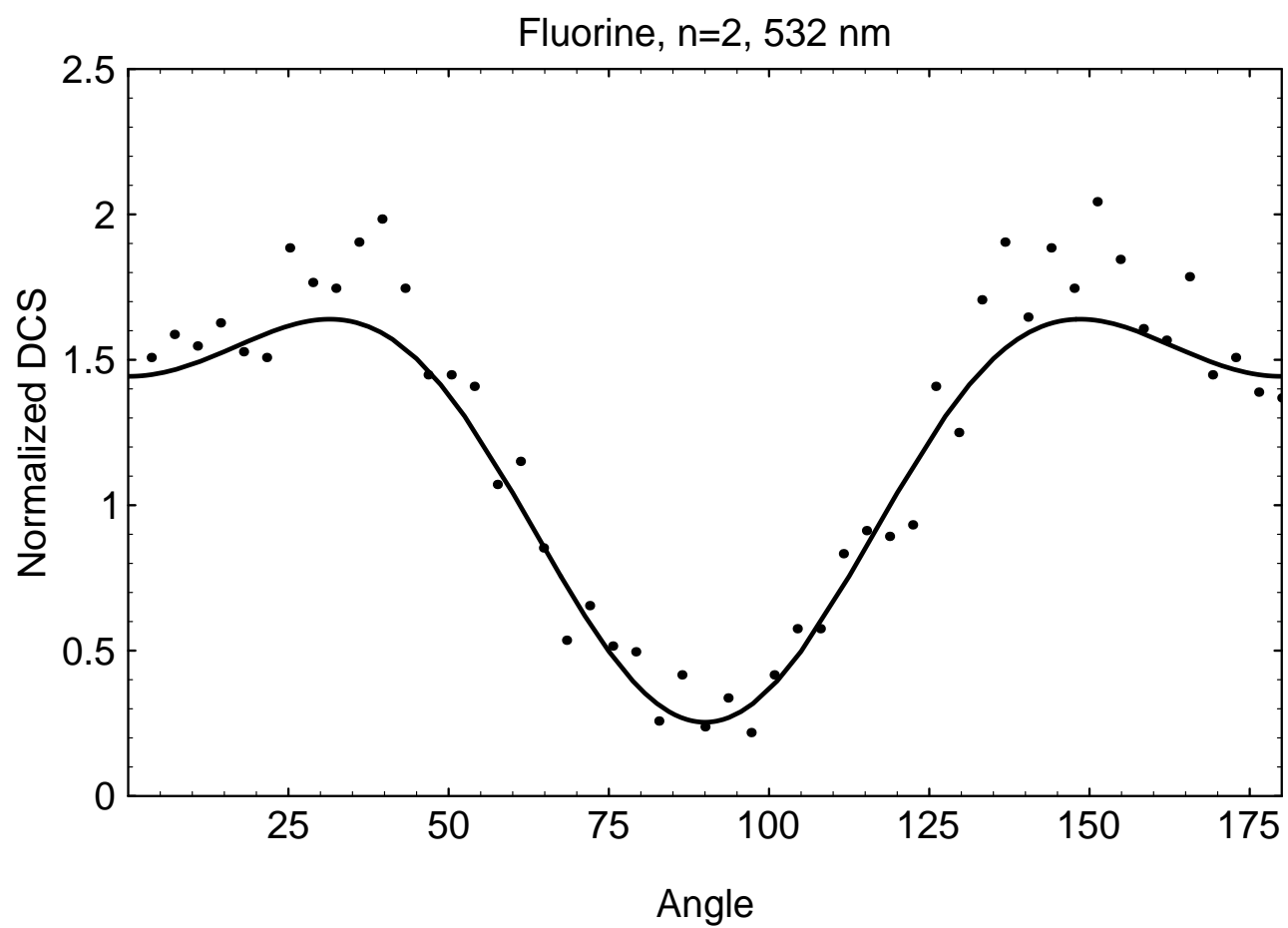
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